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Invention: SOLVENT PULPING OF BIOMASS

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SOLVENT PULPING OF BIOMASS

BACKGROUND AND SUMMARY OF INVENTION

[0001] Solvent pulping is a well known, though heretofore economically impractical, technique for producing cellulose pulp, primarily from wood-based cellulose (although it has been known to produce cellulose pulp by solvent pulping wheat straw and reed). The term "solvent pulping" as used herein means pulping cellulose material using organic cooking chemicals, such as (but not restricted to) aliphatic alcohols (e.g., methanol, ethanol, tert-butanol, and isopropanol) with or without a small amount of a mineral or organic acid, carboxylic acids with or without hydrogen peroxide, formic acid, sulfuric acid or other mineral acids, and/or acetic acid (with the effective component of the cooking liquor peracetic acid).

[0002] The economic problems associated with solvent pulping have been the inability to recover a high enough percentage of the cooking liquor effective component (e.g., alcohol), the increased COD pollution as a result of the discharge of the unrecovered cooking liquor effective component, the need for significant amounts of purchased power for electricity or steam, and the need to build-in high levels of safety into the process in view of the volatility of the cooking liquor effective component. Also, technical and/or market problems with lignin or other chemical (such as furfural) recovery for sale (often necessary for there to be any chance that solvent pulping will be economical) have been common.

[0003] According to one aspect of the present invention, solvent pulping is utilized in a manner that has a higher level of probability of being economically practical than past attempts. This higher probability results from a high level of recovery of solvent, the use of cheap raw material, and the equipment and process designs that are recognized and utilized according to the invention. The equipment utilized is all commercially available and of

proven design, yet put together in a highly efficient and effective manner. The cellulose fiber produced may be used for any purpose that pulped wood fibers are typically used, such as pulp manufacture, packaging materials, or dissolved pulp and other materials (including lignin and furfural) may be recovered.

[0004] The raw material comprises cellulose-containing biomass, and desirably biomass that would typically be a waste or minor use product. The invention may use any known or subsequently developed suitable cellulose-containing biomass including (without limitation) kenaf, whole industrial hemp stalks, bamboo, agricultural residues (the byproducts of annual food and fiber production) such as the straw of various grains, cereal grasses (such as corn), flax, cotton linters, bagasse (sugar cane pulp), banana stalks, and pineapple residue. The biomass that is desirable is a chopped, crushed or shredded version – e.g., to a maximum particle dimension of about one inch. For some agricultural residues such as corn stovers, it can be advantageous to discard roots and kernels.

[0005] Some of the possibly utilized equipment and process designs according to the present invention include:

- Using simple, but effective blow-back prevention upon upset conditions;
- Gradually stepping up the pressure and temperature in the system and process from atmospheric and ambient to high levels (e.g., to about 20-35 atmospheres, similar to U.S. Patent 4,100,016, the entire content of which is hereby incorporated by reference in its entirety, and preferably to about 350-500 psig, and above-kraft temperatures, preferably between about 180-210 degrees C) necessary to properly delignify the raw material;
- Using simple, highly reliable, equipment to provide pressure and temperature step-up, while performing different functions (e.g., steaming and impregnation);

- Indirectly heating the cooking liquor in order to maintain precise control over the solvent to material ratio and to allow the use of lower pressure steam;

- Extending delignification from a pre-hydrolysis reactor to one or more pressurized vessels while initiating washing and substantially precluding re-deposition of lignin (that is precipitating of the lignin back on the cellulose fibers);

- Minimizing energy and liquor losses by controlled hot liquor flashing;

- Providing for proper nitrogen purging where necessary during start-up or shut-down;

- Providing flexibility in the type of pre-hydrolyzing reactor utilized; and

- Providing for uniform treatment of the material.

The method of the invention is preferably, although not necessarily, practiced continuously.

[0006] In the following description, one embodiment of the method and apparatus will be described with respect to delignification of agricultural residues, e.g., straw of various grains, cereal grasses (such as corn stovers), flax, cotton linters, bagasse (sugar cane pulp), banana stalks, and pineapple residue, using ethanol as the primary solvent (e.g., about 40-60% ethanol with water (and dissolved solids), and possibly a catalytic amount of a mineral (e.g., hydrochloric or sulfuric) or organic (e.g., formic or acetic) acid). The pressures, temperatures, and other conditions mentioned are particularly advantageous for this type of raw material and solvent. However, it is to be understood that the invention is not so limited, but rather may use any known or subsequently developed solvent, and any suitable cellulose-containing biomass including (without limitation) kenaf, whole industrial hemp stalks,

bamboo, agricultural residues (the byproducts of annual food and fiber production) such as the straw of various grains, cereal grasses (such as corn), flax, cotton linters, bagasse (sugar cane pulp), banana stalks, and pineapple residue.

BRIEF DESCRIPTION OF THE DRAWINGS

[0007] Figures 1A, 1B and 1C schematically show a biomass pulping system having a vapor phase (downflow) prehydrolysis reactor.

[0008] Figure 2 schematically shows a biomass pulping system having a hydraulic (upflow) prehydrolysis reactor.

[0009] Figure 3 shows an alternative portion of a biomass pulping system.

[0010] Figure 4 shows an alternative portion of a biomass pulping system using a hydraulic (upflow) prehydrolysis reactor.

[0011] Figures 5 and 5A-5E show an alternative portion of a biomass pulping system.

[0012] Figure 6 shows a block diagram of a biomass pulping system.

[0013] Figure 7 shows a block diagram of a biomass pulping system.

DETAILED DESCRIPTION OF INVENTION

[0014] Figures 1A, 1B and 1C schematically illustrate one exemplary form (and variations) a system can take for practicing an advantageous solvent pulping method according to the invention. Figures 2, 1B and 1C schematically illustrate another exemplary form (and variations) a system can take for practicing an advantageous solvent pulping method according to the

invention. Figures 3, 4, 6 and 7 illustrate other embodiments (for example, possible changes to Figures 1A, 1B, 1C and 2, or separate systems) that may be utilized according to the present invention. FIGURE 5 schematically illustrates another exemplary form a system can take for practicing an advantageous solvent pulping method according to the invention.

[0015] In FIGURES 1A, 1B, 1C, 2, 3, 4, 6 and 7, many of the components are similar (e.g., components 23 and 94 – plug or compression screw feeders, components 24 and 98 – steaming vessel or inclined steaming vessel, components 25 and 102 – plug or compression screw feeders, components 28 and 104 – inclined impregnation screw conveyor) and have similar connections and processing conditions.

[0016] Major preferred components of the inventive systems include an ambient/atmospheric biomass feed 10, steaming (with pressure step-up) equipment 11, a combined safety barrier and pressure step-up device 12, impregnation, pressure step-up and charging equipment 13, a prehydrolysis main reactor 14 (or downflow, upflow, multistage or inclined reactor 105, or downflow reactor 107), subsequent pressurized delignifying and wash-initiating (and delignification-continuing) equipment 15, controlled solvent heating equipment 16, and delignified cellulose pulp washing equipment 17 (also referred to as solvent or alcohol washing system or equipment – which comprises conventional equipment). Other types of equipment and apparatus are utilized with these major components to get desired results.

[0017] The drawings use conventional abbreviations and symbols. For example, valves with a "PC" designation are pressure controlled, those with an "LC" designation are level controlled, those with a "TC" designation are temperature controlled, and those with an "FC" designation are flow controlled. Similarly, sensors sense temperature, level, and density, etc.

[0018] The biomass feed 10 may comprise a simple conveyor 20 that deposits particulate agricultural residues (e.g., corn stovers having a

maximum particle dimension of about one inch, and a bulk density of about 8-9 b d lbs./cu.ft.) into a conventional screw feeder airlock 21. The particulate is at substantially ambient temperature (e.g., 25 degrees C) and atmospheric pressure until fed by the feeder 21 to the presteaming bin 22. An airlock is utilized to preclude ethanol vapors from exiting the bin 22.

[0019] The steaming equipment 11 includes the bin 22, the screw 23, the equipment 12, and the horizontal steaming vessel 24. The steaming that occurs in bin 22 and vessel 24 removes air from the biomass, and may be practiced using low pressure steam (e.g., at about 50 psig). The bin 22 is preferably a DIAMONDBACK® chip bin sold by Andritz Inc. and disclosed in U.S. Patents 6,325,888, 5,500,083 and 5,628,873, the entire contents of which are incorporated herein by reference. DIAMONDBACK vessels have single convergence and side relief. This structure has no or few moving parts or flexible seals, making it particularly suitable for keeping air out and preventing ethanol leakage. Alternatively, bin 90 (in Figure 3) is preferably a live bottom chip bin, with atmospheric feed of Hammermilled cellulose-containing biomass. Steaming in bin 22 is substantially atmospheric and for about 10-30 minutes. Steaming in vessel 24 (or 98 - inclined) is for a short period of time and preferably super-atmospheric (e.g., about 2-50 psig, preferably about 10-15 psig), and the biomass is at about 100 degrees C when it enters vessel 24. The steaming in vessel 24 may take between about 30 seconds to about 5 minutes at about 2-50 psig, e.g., about 1 minute.

[0020] A wide variety of different types of equipment may be utilized for the pieces of equipment 23 (or 94) and 24 (or 98). In one embodiment, device 23 (or 94) is a plug screw feeder/compression screw device (for example, a MSD Impressafiner® sold by Andritz Inc.), or a variable speed metering screw. The rate set by 23 determines system retention time, and is used to determine proper solvent usage, and proper cooking temperature. The vessel 24 or 98 is preferably a conventional horizontal or inclined

steaming vessel (e.g., having a screw conveyor), also available from Andritz Inc., preferably utilizing medium pressure steam, e.g., about 250 psig).

[0021] The device 12 performs both a safety function and a feeding, gradual pressure step-up function. The device 12 (and all equipment downstream of it until the blow tank) is capable of withstanding the maximum pressure that may exist in the biomass containing portions of the system (e.g., in the reactor 14). The typical pressure in reactor 14 is between about 350-500 psig or lower, therefore the device 12 should be designed to withstand a pressure of 550 psig or lower, which will prevent blowback in case of an upset condition, and in general will preclude ethanol (or other solvent material) from escaping back through the feed system. While other devices can be utilized (including having the separate functions the device 12 performs), the device 12 desirably comprises a conventional Andritz rotary valve 96, only constructed to withstand 550 psig or lower. Such a valve allows continuous efficiently controlled feeding of biomass into the pressurized components of the system without unduly compressing, fiberizing, or damaging the material conveyed.

[0022] Downstream of the steaming vessel 24 (or 98) is device 25 (or 102), a plug/compression screw feeder (for example, a MSD Impressafiner® sold by Andritz Inc.). The device 25 forms a compressed plug capable of obtaining about a 200 psig pressure increase. The plug so formed also provides an excellent vapor barrier so that little or no material (e.g., ethanol) can pass back through it. Any excess moisture in the biomass is squeezed out in device 25 (or 102), and removed through a screen assembly 26 in the bottom of the device 25. The consistency of the material discharged from device 25 may be monitored using the drive motor load, with a typical consistency between about 40-60% od. The pressure of the material discharged from device 25 is preferably about 200 psig. A conventional fluffer 27 is preferably provided at the discharge of the device 25.

[0023] In alternative embodiments like Figures 3, 4 and 6, and similar to the above, downstream of the vessel 98 is device 100, a conventional screw feeder, then device 102, a compression screw device (for example, a MSD Impressafiner® sold by Andritz Inc.). The device 102 forms a compressed plug. The plug so formed also provides an excellent vapor barrier so that little or no ethanol can pass back through it. Any excess moisture in the biomass may be squeezed out in device 102, and removed through a screen assembly in the bottom of the device 102. The consistency of the material discharged from device 102 may be monitored using the drive motor load, with a typical consistency between about 40-60% od. The pressure of the material discharged from device 102 may be about 200 psig.

[0024] In the embodiments depicted in Figures 3, 4 and 6, the material preferably passes to chip bin 90, optionally to a screw conveyor 92, to a compression screw device 94, to a rotary valve 96, to an inclined steaming vessel 98, to an optional screw feeding device 100, to another compression screw device 102 (with solvent added at line 29 after the discharge from device 102), to an inclined impregnation vessel 104, and (in Figure 3) to an optional fluffer (not shown) and to reactor 14, or (in Figure 4) to an optional chip tube 81, to a screw feeding device 82, and to the bottom/inlet of reactor 80.

[0025] Preferably, there are at least two preheaters 30 and 37 in the system. One preheater 30 preheats the solvent added to the feed system. The other preheater 37 "tops off" the heat required to go to the impregnation equipment 28 to the reactor 14 temperature, but more importantly, provides additional heat to raise the temperature of the pressed pulp and the liquor drained from the second plug screw feeder 25 (or 102) up to the reactor temperature. This temperature increase is required because the impregnation equipment must operate at a lower pressure than the reactor because a single stage plug screw feeder can only generate a pressure of about 200

psig, thereby limiting the allowable temperature in the impregnation equipment to avoid flashing.

[0026] The impregnation equipment 13 of Figure 1A includes an inclined screw conveyor 28 (or 104 in FIGURES 3, 4 and 6). Cooking liquor (e.g., preferably about 40-60% ethanol, most of the remainder being water (and dissolved solids) with perhaps a small amount of acid) is added to the biomass in or before device 28 (or 104). In some of the exemplary embodiments illustrated, the cooking liquor in line 29 is indirectly heated by medium pressure steam in the indirect heater 30 and then fed to the conventional fluffer 27 (or at the discharge of 102), which substantially uniformly mixes the biomass and cooking liquor so that uniform impregnation occurs. Medium pressure steam may be added directly to the device 28 (or 104) via line 31 as long as the amount of liquid that will result from the steam is considered in determining the constituents of the cooking liquor, and the proper liquor-material ratio. For the process of the invention, it is desirable that the liquor-material ratio be high, e.g., between about 5:1 to 9:1 (e.g., about 6:1). In one embodiment, impregnation typically takes between about 30 seconds and 5 minutes (e.g., about 1 minute) at about 200 psig.

[0027] According to the embodiment depicted in Figure 1A, from the inclined screw feeder 28, the biomass passes to another plug screw feeder 32 where the pressure is increased to digesting pressure. For many solvent pulping operations, including with ethanol as the primary cooking liquor, the pressure is preferably increased to between 300-425 psig, more preferably about 350-400 psig. Passage of the biomass through the plug screw feeder 32 in the presence of cooking liquor greatly increases the penetration rate of the solvent into the biomass due to the flexing and working of the material in the presence of the active cooking chemical. Any drainage from the feeder 32 passes through a screen, into line 33 and is returned to the system. A second fluffer 34 may be provided at the discharge of the feeder 32, and the biomass is discharged by fluffer 34 into the prehydrolysis reactor.

[0028] The controlled solvent heating equipment 16 is connected to the line 33, and may include tank 35, pump 36, and indirect continuous circulation heater 37. The recirculated liquid from line 33 is heated in heater 37 (e.g., to about 210 deg. C if the desired cooking temperature is about 200 deg. C) and then re-mixed with the biomass. The heated re-circulated cooking liquor may be re-mixed by adding it in lines 38 to the feeder 32 just before and at the second fluffer 34. This heating and re-mixing allows the biomass to reach the final desired prehydrolysis temperature (e. g. between about 180-210 deg. C). The system 16 achieves this desirable result with the use of lower pressure steam (250-325 psig) than would be necessary if steam were directly added to the biomass. That is, lower pressure steam than otherwise would be necessary (the otherwise necessary steam would be at a pressure of 400-500 psig) may be used in the heater 37. For this reason, and to keep excess water out of the system, the makeup cooking liquor (typically ethanol), and, if required, water, are also preheated (in indirect heater 30) before addition to the cooking circulation.

[0029] According to an embodiment as depicted in Figure 3, from the inclined screw feeder 104, the biomass can be passed to an optional fluffer 34 (like in Figure 1A) at the discharge of the impregnation device 104, and the biomass is then discharged to a conventional reactor 105. For many solvent pulping operations, including with ethanol as the primary cooking liquor, the pressure is increased to between 300-425 psig, preferably about 350-400 psig. Any drainage from feeder 100 may pass through a screen, into line 33 and can be returned to the system.

[0030] According to the exemplary reactor feed system of Figure 3 from bin 90 to feeder/conveyor 104 (read in conjunction with Figure 1A and as an alternative to the reactor feed system from bin 22 to feeder 32 in Figure 1A), the controlled solvent heating equipment 16 is optionally not used (including recirculation line 33 to line 38). In the exemplary embodiment of Figure 3, the reactor 105 can be one of many commercially available reactors with

associated equipment, e.g., an upflow, downflow, multi-stage or inclined reactor with associated equipment that is commonly known and commercially available.

[0031] In the embodiment illustrated in Figure 1A, the continuous prehydrolysis reactor 14 is a vapor phase continuous downflow ethanol-biomass reactor (digester). The reactor 14 includes a substantially vertical vessel shell 39 having an inlet 40 at or adjacent the top thereof and preferably directly connected to the outlet from the second fluffer 34, and an outlet 41 at or adjacent the bottom thereof. A vapor phase 42 is maintained at the top portion of the reactor 14 as seen in Figure 1A, and typically some biomass – shown schematically at 43 – is in a generally conically shaped pile in the vapor phase 42. A gamma gauge, or the like, senses and assists in controlling biomass level, while a dp cell, or the like, senses and assists in controlling liquid level. Off-gases are vented by the conventional vent 44. For start-up and other conditions requiring safety procedures, a nitrogen purge is provided for the vessel 39, as indicated schematically by line 45 and the associated pressure controlled valve illustrated in Figure 1A. Additionally, this control scheme may be used to control an "overpressure" situation under normal operations.

[0032] The cooking liquor (ethanol) and biomass move downwardly substantially concurrently in the vessel 39, and some delignification of the biomass occurs. While alkaline delignification can be practiced, preferably the pH in the vessel 39 is about 4-5, and the consistency within the vessel is between about 10-30% solids at the beginning of the process and 5-20% solids at the finish. Somewhat spent cooking liquor is extracted by extraction screen 46 just above outlet 41, and part of the extracted liquor is passed in line 47 to the flash tank 48 (Figure 1B), while another portion 47' is recirculated via line 49 to the indirect heater 37. Some of the liquid from the pressurized filtrate tank 63 can be flashed for ethanol recovery, as by passing it in line 49' and combining it with line 47, to pass to flash tank 48. A

conventional rotating scraper 50 is preferably provided at or adjacent the outlet 41 of vessel 39 to prevent pluggage of the vessel 39, and to help provide substantially uniform movement of biomass through the reactor 14.

[0033] Unlike a conventional kraft continuous digester, the reactor 14 provides no countercurrent wash within the vessel 39 because the biomass material (and particularly for corn stovers) is not reliably permeable enough. Rather washing, and further delignification, are provided in subsequent vessels. In the preferred embodiment illustrated in Figures 1A and 1B, external wash-initiating and delignification-continuing equipment 15 is provided in the form of first and second series-connected conventional pressure diffusers 51, 52, respectively. This allows ethanol extraction to occur in stages, with successively cleaner solvent, while the pressure diffusers 51, 52 are part of a modified cooking system in much the same way that a digester wash zone is part of a modified cooking system in a continuous kraft digester. The pressure diffusers 51, 52 (and optionally 64) are preferably conventional pressure diffusers available from Andritz, but are designed to withstand pressures of 500 psig, or even higher, and at least 450 psig for purposes of the present invention.

[0034] The wash/delignification liquor (diluted ethanol) in the first diffuser 51 is added in line 53, from the filtrate tank 54 connected to the liquid discharge 55 from the second diffuser 52. For the second diffuser 52, however, the wash/delignification liquor introduced at 56 will be cleaner, not only including filtrate from the filtrate tank 57 from the external wash system 17, but also fresh ethanol from line 58 from the solvent recovery tank 59. The liquor added at 56 is heated in indirect heater 60 to approximately the same temperature as in the main reactor 14 (e.g., about 180-210 degrees C, but perhaps between 100-200 degrees C).

[0035] Desirably, first and second retention tubes 61, 62, respectively, are provided after each of the diffusers 51, 52. The retention tubes 61, 62 let freshly extracted lignin diffuse out of the biomass fibers after each diffuser 51,

52, and before the subsequent treatment stage, greatly reducing lignin re-precipitation. The volume of the tubes 61, 62 (given a substantially constant material flow rate through the system) will determine the retention time, preferably between about 1-10 minutes (e.g., about 5 minutes) for corn stovers.

[0036] The use of pressure diffusers 51, 52 allows the process to be continuously (without reduction) operated at very high temperature and pressure without disadvantage. By maintaining high super-atmospheric pressure and elevated temperature, it is possible to keep ethanol vapors contained in a manner that cannot be obtained with other conventional washing equipment. Also, filtrate tanks (e.g., 54, 57, 63) between stages can be fully pressurized (e.g., between about 350-425 psig) so as to prevent hot liquor from flashing between stages, and to reduce or minimize pumping power and difficulty. Pressurized filtrate tanks are possible because of the use of the pressure diffusers 51, 52 and 64 (for the washing equipment 17, 17' or 17a). It may be possible to operate the desired process without the filtration tanks.

[0037] After the second retention tube 62, the pulp is discharged to a conventional blow tank 65 (Figures 1B, 1C and 6); that is, the pressure of the pulp is substantially instantaneously greatly reduced (perhaps even to about atmospheric) while hot liquids flash. It may be possible to operate the blow tank at about 15 psig as well as to operate with an MC® pump at the discharge of the tank. An MC® pump 72, available from Andritz Inc. or other suitable pump for pumping a slurry with a large percentage of solids, may be used to pump the pulp to the system 17, 17' or 17a. In blow tank 65, a portion of the ethanol is flashed into a relief condenser 66 (while simultaneously pre-heating process water, e.g., for making cooking liquor or steam), and then recycled via line 67 for reuse (e.g., at the impregnation stage). By this point, the amount of lignin has been significantly reduced so that it will not precipitate onto the cellulose fibers even though the concentration of ethanol

and the temperature have dropped significantly, and the pH has decreased, as a result of flashing and washing.

[0038] The third pressure diffuser 64, in system 17, washes the pulp and facilitates ethanol (or other solvent) recovery. The diffuser 64 is designed to reduce the amount of ethanol left in the pulp after flashing by about 90%. The removed ethanol is circulated in line 68 to the filtrate tank 57, to be used as wash/delignification liquor for the second diffuser 52. The wash liquor for diffuser 64 preferably comprises substantially clean water, introduced at 69. The extracted pulp in line 70 may be sent to storage, or immediately bleached or otherwise treated, and ultimately may be used for making any products that pulped wood fibers (or, depending upon the biomass source, other cellulose pulp) are typically good for manufacturing.

[0039] Instead of a single pressure diffuser 64, washing in stage 17 may be accomplished using a plurality of pressure diffusers, or four or more stages of other conventional types of washers, or combinations thereof depending on the degree of solvent recovery desired and the level of loss than can be allowed. As shown in Figure 7, one set of pressure diffuser 51 and retention tube 61 is used before the blow tank 65 followed by the vessels for multistage alcohol (solvent) washing 17a (which are conventional washing equipment and associated piping).

[0040] The unique system and embodiments of the subject invention allow highly beneficial recirculation of solvent, allows the use of lower pressure steam, reduces water entering the system that keeps the evaporation needs of the final product lower and that results in the need for less solvent to maintain proper solvent concentration.

[0041] As noted above, Figure 2 illustrates another embodiment that may be utilized according to the present invention. In Figure 2, all of the components are preferably similar to those in Figure 1A (and designated by

the same reference numerals), except that an upflow hydraulic prehydrolysis reactor 80 is used.

[0042] As also noted above, Figure 4 illustrates another embodiment that may be utilized according to the present invention. In Figure 4, most of the components are preferably substantially the same as in Figures 1 and 2 (components 23 and 94, components 24 and 98, components 34 and 100, components 25 and 102, components 28 and 104) and have similar connections, except the different sequence of the components and the use of a live bottom buffer bin 90 instead of bin 22. For the system depicted in Figure 4, the operation is similar to that described above for Figure 3, except an upflow hydraulic prehydrolysis reactor 80 and optional components (81 and 82) are used, similar to the system depicted in Figure 2.

[0043] As is conventional for upflow reactors, a "chip tube" (available from Andritz Inc.) 81 can receive the slurry of biomass and cooking liquor that is to be introduced into the reactor 80. In this case, the slurry can originate from a second, optional fluffer 34, as in Figure 2. A screw feeder 82 may be used to transport the ethanol-biomass slurry from the chip tube 81 to the inlet 83 of the reactor 80 to flow upwardly in the hydraulic reactor 80. The extraction screen 46 is adjacent the outlet 84 of the reactor 80, near the top thereof, as is the scraper 50.

[0044] As further noted above, Figure 6 illustrates another embodiment that may be utilized according to the present invention. Figure 7 illustrates another embodiment that may be utilized according to the present invention. In Figures 6 and 7, all of the components are preferably similar to those in Figures 1A and 3 (and designated by the same reference numerals), including the use of a downflow reactor. Hammermilled cellulose-containing biomass material passes (via atmospheric feed) to chip bin 90, optionally to a screw conveyor 92, to a compression screw device 94 (e.g., a MSD Impressafiner® available from Andritz Inc.), to a valve 96, to an inclined steaming vessel 98 (utilizing medium pressure steam, e.g., at about 250 psig), to an optional

screw feeding device 100, to another compression screw device 102 (e.g., a MSD Impressafiner® available from Andritz Inc.), with solvent (e.g., ethanol) added at line 29 after the discharge from device 102 (e.g., at the outlet of device 102 – meaning at the outlet per se or near the actual outlet and before the impregnation vessel 104), to an inclined impregnation vessel (screw conveyor) 104, to a conventional downflow reactor 107 (like reactor 14 in Figure 1A), to a pressure diffuser 51 (at full reactor temperature and pressure, e.g., about 180 to 210 degrees C and about 350 to 500 psig), to a retention tube 61 (for additional reaction time), to a pressure diffuser 52 (at full reactor temperature and pressure, e.g., about 180 to 210 degrees C and about 350 to 500 psig), to a retention tube 62 (for additional reaction time), to a conventional blow tank 65 (with an optional scraper), for example, at atmospheric pressure and at a boiling point of about 75 to 100 degrees C (when using ethanol, because the boiling point of ethanol and water), to a pump 72 (e.g., an MC® Pump available from Andritz Inc.), to conventional vessels for multistage alcohol washing system 17a. Unlike Figure 6 (which discloses at least two sets of pressure diffusers and retention tubes – and more of which can be utilized), Figure 7 only shows one set of a pressure diffuser and a retention tube.

[0045] In this embodiment of the invention, like the other embodiments, the compression screw feeders 94 and 102 form a plug of material at discharge to effectively block or hinder the back passage of solvent or solvent exhaust. In another aspect of the invention, the retention tubes 61 and 62, at least one of which is utilized in the systems, processes and methods of the invention, in conjunction with the pressure diffusers 51 and 52, at least one of which is utilized in the systems, processes and methods of the invention, greatly assist with the final stages of cooking and the initial stages of washing of the material. This assists in allowing the use of a smaller reactor/digester 107 (or 105 in Figure 3), i.e., the bottom half of a digester is not necessary for washing due to the washing capabilities of the pressure diffuser(s) and

retention tube(s). In this regard, a retention tube is a wide space in the processing line where lignin continues to dissolve.

[0046] Figure 5 illustrates an additional embodiment that may be utilized according to the present invention. This embodiment is particularly useful for low production rate cases, but could be used for a wide range of production rates. While a system using two screw conveyors is described, it should be noted that any number of screw conveyors could be used.

[0047] The embodiment illustrated in Figure 5 relates to the feed system, which may be operated in a continuous manner. Biomass is fed to a bin, such as a live bottom bin 200. This bin may be over sized to allow for up to 8 hours of retention time. The bin also may be large enough to allow for the immediate condensation of any ethanol or other solvent used in the pulping, if such solvent should back into the bin from the downstream equipment, rather than releasing the solvent to the atmosphere. Preferably, two independently operated metering screws 201, 202 equipped with variable speed drives may be located in the bottom of the live bottom bin to remove the biomass from the bin in a controlled fashion at a specified rate. Only one metering screw may be turning at any given time.

[0048] Material from each metering screw 201, 202 may be discharged into a separate screw conveyor 204 (SC#1), 205 (SC#2) which functions as a biomass pretreatment vessel. Preferably, the system may contain two such vessels, one for each metering screw 201, 202, and they may be operated in parallel with the operating cycles offset in time. Each screw conveyor 204, 205 may be equipped with inlet and outlet isolation valves, a variable speed drive and revolution counter, inlet distribution headers for the addition of steam, solvent, and inert purge gas, a vent header for the collection and removal of purged air and other gases, and temperature and pressure measurement instrumentation. The screw conveyors 204, 205 may be operated on alternating cycles such that one conveyor is always emptying pretreated biomass, at the desired production rate, into a feed chute 210

located above an inclined impregnation vessel (IV) 214. A mixer 212 may be located between the feed chute 210 and the IV 214. From the feed chute forward, the system may be operated in a continuous manner at a uniform production rate. The conveyor(s) which is <u>not</u> conveying biomass material into the feed chute may be utilized in a batch mode to carry out the other required pretreatment operations, as detailed in the table below. These operations may include uniformly filling and isolating the conveyor, steam purging the biomass in the conveyor to remove all air, heating the biomass to the desired pretreatment temperature, impregnating the biomass with the desired amount and concentration of water-solvent mixture preheated to the desired pretreatment temperature, pressurizing the conveyor with N2 (232) or other inert gas up to the feed chute pressure and opening the discharge valve 220, 221 between the conveyor 204, 205 and the feed chute 210, isolating the conveyor 204, 205 after the biomass has been conveyed into the feed chute 210, depressurizing the conveyor 204, 205 by venting it to a condenser 208, and steam purging the conveyor 204, 205 to remove any residual solvent vapors.

[0049] The entire operating cycle for one conveyor may take approximately 70 minutes, and may consist of 8 individual steps, as follows:

[0050] Step 1(~5 minutes): The screw conveyor (SC) inlet valve 203, 233 is opened and the metering screw 201, 202 and SC's 204, 205 are started in order to transfer biomass from the live bottom bin 200 into the screw conveyor 204, 205. The screw conveyor rpm rate is set so as to have the biomass distributed along the entire length of the conveyor 204, 205 in the allotted fill time. A conveyor shaft revolution counter is used to determine when the biomass material has moved along the SC 204, 205 to the discharge point 206, 207. The metering screw speed is set to fill the SC 204, 205 to the desired level along its length, and is ratioed to the desired production rate and the SC conveyor speed. At the end of step 1, the SC 204, 205 and metering screw 201, 202 are stopped and the inlet valve 203,

233 to the SC 204, 205 is closed, isolating the SC 204, 205 from the metering screw 201, 202 and the live bottom bin 200.

[0051] Step 2 (~ 5 minutes): When the SC 204, 205 is isolated, low pressure steam (about 5-30 psig) is used to purge any air in the biomass material through a vent line to a relief condenser 208.

[0052] Step 3 (~ 5 minutes): After purging the air from the system, the relief valve 238, 240 is closed. Steam continues to be added to the SC 204, 205 until the system is up to the desired preimpregnation temperature, approximately 280-300 degrees F. At this point, the hydrolysis reactions between the solvent and biomass are still very slow, so the retention time in the SC 204, 205, which will vary between material located near the inlet and the outlet of the SC when the material is conveyed out of the SC 204, 205, does not adversely affect the uniformity of treatment. The steam (230) used in this step is preferably about 75-150 psig steam.

[0053] Step 4 (~5 minutes): Preheated water and solvent mixture is added to the SC 204, 205 through a spray header 216, 217 along the top of the SC to preimpregnate the biomass prior to pressurization with N2 (232) or other inert gas (next step). The amount of each liquid is adjusted for the desired liquid to biomass ratio, the initial biomass moisture, the steam condensed in the SC 204, 205, and the anticipated condensation of steam and ethanol vapor to be later added in the impregnation vessel to bring the biomass up to the desired final reaction temperature prior to entering the reactor.

[0054] Step 5 (~ 5 minutes): Next, the SC 204, 205 is brought up to the IV feed chute pressure by adding a pressurized inert gas such as N2 232. The pressure is monitored in the SC 204, 205, and the final pressure is adjusted using a DP cell to measure the differential pressure between the SC 204, 205 and the feed chute 210 to ensure close control before opening the SC discharge valve 220, 221.

[0055] Step 6 (~35 minutes): When the SC 204, 205 and IV feed chute 210 pressures are equal, the SC discharge valve 220, 221 is opened. When the other screw conveyor (SC #2) 205 has finished transferring its supply of biomass to the IV feed chute 210, the SC (SC#1) 204 is started and set at the desired production rate. The biomass is then steadily transferred into the IV feed chute 210 until SC #1 204 is empty, at which time SC #2 205 will again be ready to transfer material into the feed chute 210. As a result, the IV feed chute 210 receives a steady and continuous influx of material throughout the entire cycle, even though the SCs 204, 205 may be operated in a semi-continuous manner. This enables the rest of the system to also operate in a stable, continuous manner. During step 6, a small amount of N2, or other inert gas, purge may be added to the inlet end of the SC 204, 205. This keeps hot vapors from diffusing back into the SC 204, 205 and prematurely heating the biomass and solvent near the inlet of the SC, resulting in uneven treatment of the biomass.

[0056] Step 7 (~5 minutes): After all of the biomass in SC #1 204 has been transferred into the IV feed chute 210, the SC discharge valve 220 is closed, isolating the SC #1 204 from the feed chute 210. Both the total SC revolutions and the drive amperage may be used to monitor the material transfer completion. A gamma gauge at the transfer point into the feed chute can also serve as a backup control method. The N2, or other inert gas, purge is also closed at this time. After the SC 204, 205 is isolated, the relief valve 238, 240 to the condenser 208 is opened and the pressure is relieved down to ~0 psig.

[0057] Step 8 (~5 minutes): After the SC pressure has dropped close to 0 psig, the SC 204, 205 is purged with low pressure steam to the condenser to remove any traces of residual solvent before opening the SC inlet valve 203, 233 and exposing the metering screw 201, 202 and live bottom bin 200 to the vapors remaining in the SC. If desired, a brief water wash or N2 (or

other inert gas) purge can also be inserted in the cycle at this point to cool the SC, but normally this will not be necessary.

[0058] At the end of step 8, all steam, water, and N2 (or other inert gas) purges are shut off and the relief valve 238, 240 to the condenser 208 is closed. The SC pressure is checked and the DP between the SC 204, 205 and the metering screw 201, 202 is preferably at zero. The inlet valve 203, 233 may then be opened to begin another cycle.

[0059] The following Table 1 illustrates the timing of the interconnected operating cycles of SC #1 and SC #2.

[0060] After the biomass material is transferred into the IV chip chute 210, it moves down into the impregnation vessel (IV) 214, which preferably consists of an inclined screw conveyor equipped with the appropriate headers and control instrumentation. Preferably, the biomass enters the lower end of the unit and is transferred upward through the IV 214 by the action of an inclined conveyor screw. Any free liquid with the biomass maintains a liquid level set by the elevation of the overflow into the main reactor 250. The retention time in the IV 214 is about 5 minutes.

[0061] In the IV 214, the temperature of the biomass and solvent/water mixture is increased to about 380-400°F. This temperature increase is achieved by introducing a mixture of steam at about 450 psig and solvent (at a pressure of about 450 psig). A solvent boiler 252 is used to obtain the mixture of solvent and steam needed to increase the temperature of the biomass and solvent/water mixture in the impregnation vessel 214 to about 400°F. Temperature control at the impregnation vessel 214 may be used to control the quantity of steam/solvent mixture from the boiler to the impregnation vessel.

[0062] The amount of solvent and steam used for heating in the IV 214 preferably supplements the solvent introduced into the impregnation vessel from the SC 204, 205 and results in the total solvent required for the reaction. All solvent and steam needed for the reaction is preferably added prior to the biomass being fed to the reactor 250. The reactor 250 and downstream equipment used for this process may be the same as that in Figures 1A and 1B or 2.

[0063] In a commercial size installation, it may be preferable or necessary to use an inert gas circulation/recovery system.

[0064] The description given above is based on a preferred system using two parallel screw conveyors for pretreatment vessels. Two is the minimum number of SCs for this type of system, but more may be used if desired.

Reasons for using 3 or more SCs in the feed system include possible mechanical design limitations for very large SCs, cost tradeoffs between a small number of large vessels versus a larger number of smaller vessels, and the advantage of being able to take one SC off line for maintenance without interrupting the operation. The basic rule is still the same: that one SC must be steadily discharging material into the IV feed chute at all times. Thus for step 6 above, with 2 SCs, step 6 takes ½ of the total cycle time, for 3 SCs 1/3 of the cycle time, and for n SCs 1/n of the cycle time. Except for step 6, the cycle can be interrupted and held at any point if extra time is available, as for example at reduced production rates.

[0065] It is also possible to use other configurations for the pretreatment vessels rather than screw conveyors. Drag chain systems or even vertical gravity flow vessels can also be used.

[0066] The main reactor can also be any of these types of configurations. It is not necessary for the reactor to be a vertical unit. It may be an inclined or horizontal unit, equipped with either a conveyor screw or drag chain conveyor.

[0067] The impregnation vessel (IV) may also be either horizontal or inclined, and equipped with either a conveyor screw or drag chain conveyor.

[0068] Conventional or subsequently-developed techniques will be utilized to recover lignin, furfural, and other saleable commodities, from various streams from the processes described above and illustrated in Figures 1A, 1B, 2, 3, 4, 5, 5A – 5E and 6.

[0069] The equipment utilized in the systems, processes and methods of the invention can be made of any material that will stand up to the chemicals and conditions described. Preferably, the wetted components are made of 316L stainless steel, or Hastalloy C, or higher metallurgies, depending on the temperature and pH used in any particular application. Generally speaking,

lower pH's and higher temperatures will require more corrosion resistant metallurgies.

[0070] The invention is not to be limited except by the prior art. All ranges include each specific range within a broad range (e.g., 180-210 deg. C means 181-209 deg., 199-201 deg., 190-200 deg., and all other narrower ranges within the broad range). Recognized equivalents may be used where appropriate. Other conventional conditions and procedures may be used for the solvent pulping and recovery of materials too, such as shown in U.S. Patents 6,364,999, 5,865,948, 5,788,812, 5,681,427, 4,941,944, 4,764,996, 4,100,016, 3,585,104, and 1,856,567, the disclosures of which are hereby incorporated by reference herein.